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Solubility of Lead Nitrate
And Mercuric Chloride
In the Presence of
Other Soluble Chlorides

Graduate School

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SOLUBILITY OF LEAD NITRATE AND
MERCURIC CHLORIDE IN THE PRESENCE
OF OTHER SOLUBLE CHLORIDES

BY

JOHN KENYON BUSH, A.B., 1900

THESIS FOR THE DEGREE OF MASTER OF ARTS

IN THE
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May 29th 1903

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

and that of Dr. A. R. Lincoln
Mr John Kenyon Bush

ENTITLED

Solubility of Lead Nitrate and
Mercuric Chloride in the presence of other soluble chlorides

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF

Master of Arts

Arthur R. Palmer

HEAD OF DEPARTMENT OF

Chemistry

SOLUBILITY OF LEAD NITRATE AND MERCURIC CHLORIDE
IN THE PRESENCE OF OTHER SOLUBLE CHLORIDES.

The solubility of lead chloride in the presence of other chlorides has been determined by various investigators but owing to the fact that the addition of mercuric chloride to lead nitrate does not precipitate lead chloride, it was thought desirable to determine the effects of one salt on the other. If just enough of a soluble chloride be added to a solution of lead nitrate to produce a turbidity or slight precipitate, the addition of mercuric chloride will dissolve the precipitate. Lead nitrate and mercuric chloride solutions may be mixed in all proportions without the production of an insoluble chloride but the addition of a few drops of another chloride may precipitate the lead.

An investigation of the literature on this subject shows that very little has ever been done with mercuric chloride and lead nitrate jointly. Most of the data given was secured some time ago, as is shown by the date of J.C. Bell's contribution to the Journal of the Chemical Society, 1868. Ditte, in 1881, in an article written for Comptus Rendus showed the action of hydrochloric acid on lead. Noyes, however, in 1892 published the results of his investigations as to the solubility of lead chloride in the presence of other chlorides.

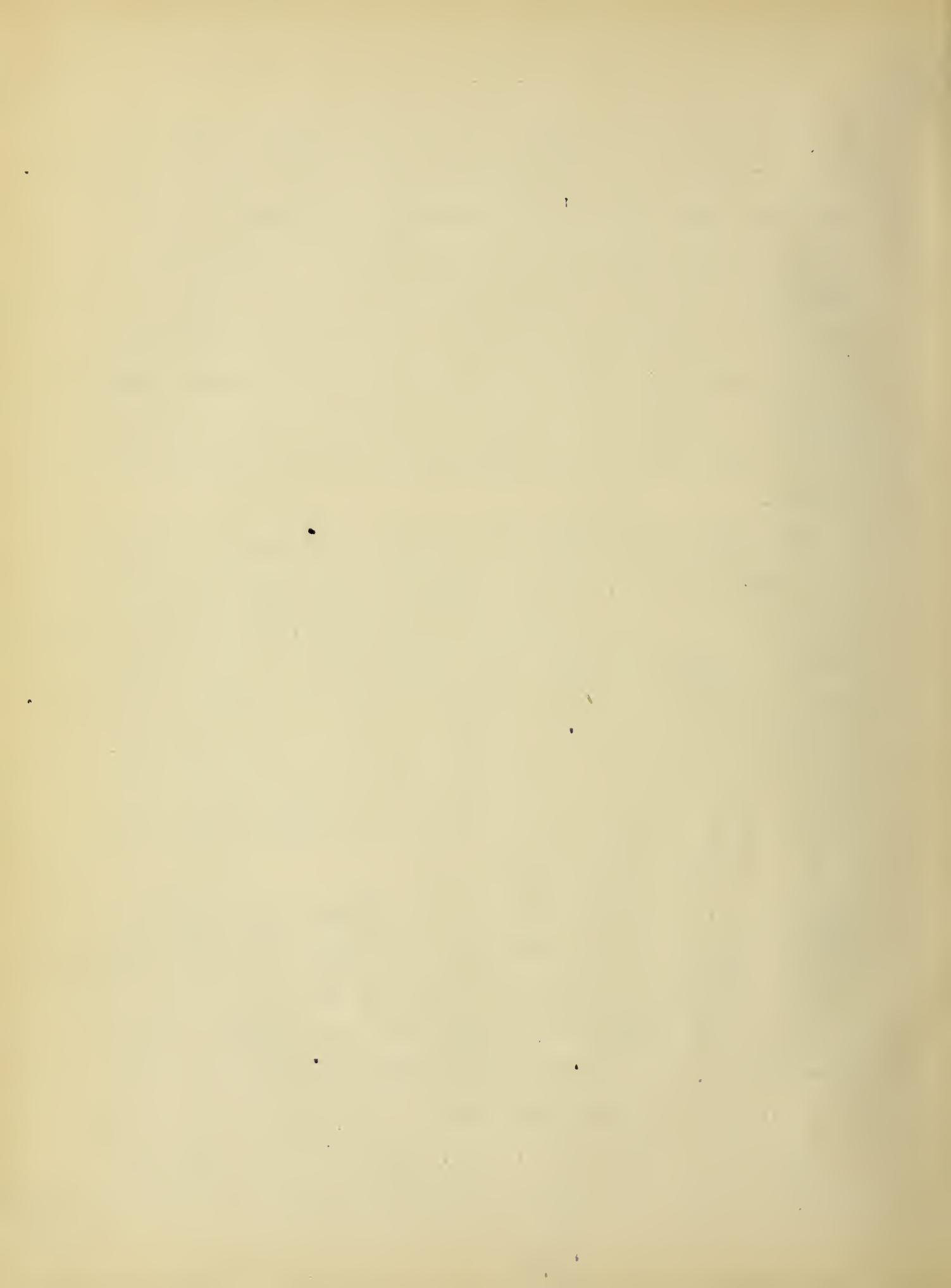
The authorities do not arrive at the same conclusions in their work, so it would be logical to accept the last determination as the most accurate were it not for a recent article by Lichty,

of the University of Michigan in which his findings agree with none of those of his predecessors. It is evident that the personal equation enters largely into investigations of this nature and the conclusions herein given indicate that the personal element influenced my results. Every precaution was taken to get accurate data and the findings in all cases are the average of at least two and generally four determinations. All the thermostat manipulations for getting the solutions at constant temperatures were run in duplicate and the analysis of each set of solutions in duplicate.

The addition of a soluble chloride to a solution of the soluble salts of silver, mercury and lead will, in general, produce a precipitate of the chlorides of these metals. There are, however, several phenomena connected with the reactions of the chlorides, worthy of more than passing notice. In the first place, if mercuric chloride be added to a lead nitrate solution no precipitate of lead chloride is produced and the proportions in which the solutions are mixed does not affect the product. In no case is an insoluble compound formed.

Secondly, if the chlorides of the alkalies, the alkaline earths, and some of the heavy metals are added to a lead nitrate solution slowly, the precipitate dissolves as fast as it is formed up to a certain point. At the point where the permanent precipitate appears there must be in equilibrium lead chloride, lead nitrate, and the chloride and nitrate of the precipitating metal.

According to Noyes (Zeit. Phys. Chemie IX, 623, 1892) lead chloride is much more soluble in pure water than in the presence



of the chlorides of the metals, no matter what the dilution. The decrease in the solubility of lead chloride in the presence of some chlorides is illustrated in the following table:

SALTS	CONCENTRATION	SOLUBILITY
H ₂ O	normal	.0777
HCl	.05	.0478
KCl	.05	.0482
MgCl ₂	.05	.0503
CaCl ₂	.05	.0503
CdCl ₂	.05	.0601

In the presence of more concentrated solutions Noyes shows that the solubility decreases with the increase of concentration.

J. Carter Bell (Jour. Ch. Soc. VI, 355, 1868) and Ditte (Comptus Rendus 92, 718) show that the solubility of lead chloride decreases with the increase in strength of the hydrochloric acid until a concentration between ten and fifteen percent is reached, when the solubility begins to increase.

Lichty (Jour. Am. Ch. Soc. XXV, 469, 1903) has recently determined the solubility of lead chloride in pure water but his results do not agree with those found by previous investigators. At zero degrees Lichty finds 0.6728 grammes of lead chloride to be dissolved by one hundred grammes of water. Bell finds 0.800 grammes at twenty-five degrees while Lichty finds 1.078 grammes. Noyes finds 0.777 grammes at twenty degrees and Bell 1.18 grammes. So even now, the solubility of lead chloride does not seem to be very accurately determined and from Lichty's method we would not infer that his

results are any more reliable than those of the others.

A series of roughly quantitative determinations of the effect of soluble chlorides on the solubility of lead chloride was made by adding to a solution of lead nitrate, solutions of the other salts. These solutions were made so that they all contained the same quantity of chlorine per litre. The solutions of the chlorides of the alkalis were twice molecular while those of the alkaline earths and the heavy metals were molecular. From these solutions were then prepared normal, half normal and tenth normal solutions. The effect of these chlorides on the solubility of lead chloride in the presence of mercuric chloride was also determined.

The method of procedure was as follows. A saturated solution of lead nitrate at twenty degrees contains 52.3 grammes per 100 c.c. of water. The molecular weight of lead nitrate is 331 therefore 633 c.c. of a saturated solution contains one gramme molecule of lead nitrate. To 6.33 c.c. of this solution, which contained one one-hundredth of a gramme molecule of lead nitrate, was added a solution of a chloride. The precipitate first produced dissolved, and the chloride was added until a sufficient amount had been introduced to produce a permanent precipitate or a decided opalescence. A saturated solution of mercuric chloride at twenty degrees contains 7.39 grammes. Since the molecular weight is 270.9 it would require 366 c.c. to furnish one gramme molecule of mercuric chloride, or 3.66 c.c. ^{to furnish} one one-hundredth of a gramme molecule.

This quantity of mercuric chloride was then added to the mixture of the other two chlorides and the opalescence or precipitate disappeared, the solution becoming perfectly clear. The soluble chloride was again added until the precipitate or opalescence

reappeared. The experiment was then repeated by mixing 6.33 c.c. of lead nitrate solution and 3.66 c.c. of the mercuric chloride solution and then adding the soluble chloride until the precipitate or opalescence appeared. The total amount of the soluble chloride was found to be the same by both methods of manipulation. The quantities of lead nitrate solution and mercuric chloride solution selected were such as would give the amount of lead and chlorine which corresponded to one one-hundredth of a gramme molecule of lead chloride, that is, in the ten centimeters of the mixture of these two solutions in the proportion stated above, there would be 2.778 grammes of lead chloride.

One centimeter of a twice normal solution of potassium chloride was required to produce a precipitate when added to six and thirty-three hundredths centimeters of lead nitrate solution. The amount of potassium chloride in this solution was 0.1492 grammes per c.c. which is equivalent to 0.0709 grammes of chlorine, or to 0.2779 grammes of lead chloride. In other words, there should be present 0.2779 grammes of lead chloride in 7.66 c.c. of this solution, or 3.79 grammes of lead chloride in 100 c.c. of the mixture. The amount of lead present in the form of lead nitrate is sufficient to produce exactly ten times this quantity of lead chloride. This amount of lead chloride remains in solution, but the subsequent addition of the soluble chloride causes the precipitation of the lead chloride.

When mercuric chloride is present in a quantity sufficient to furnish enough chlorine to precipitate all the lead as lead chloride it requires three-tenths of a centimeter more of the twice normal solution of potassium chloride to produce the permanent

precipitate of lead chloride. In the presence of mercuric chloride the lead chloride is more soluble. When a normal solution of potassium chloride is employed, exactly twice the number of centimeters were required to produce a permanent precipitate that were necessary when a twice normal solution of potassium chloride was employed. In the case of a half normal solution slightly more than twice the quantity was necessary than when the normal solution was used.

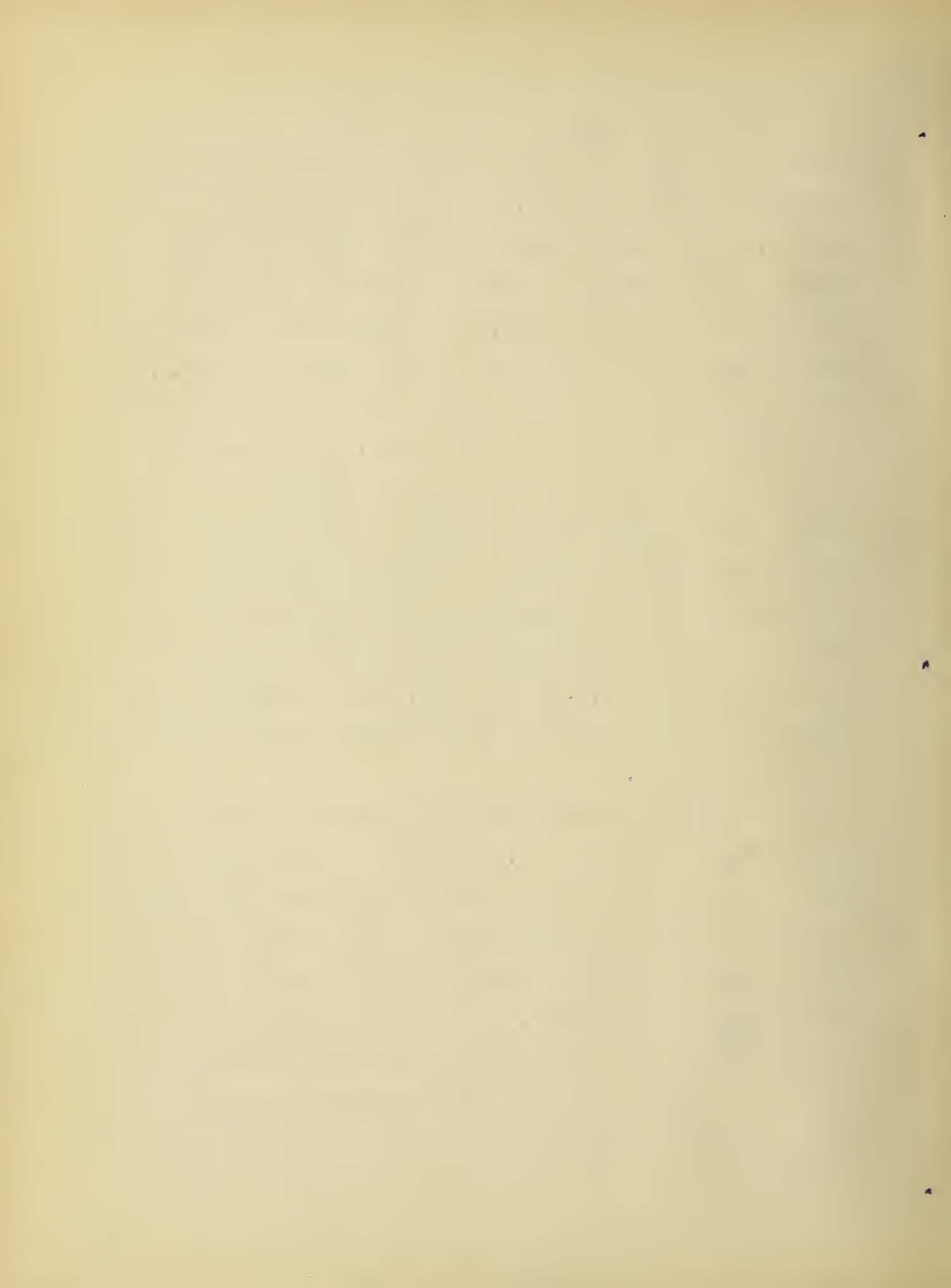
These results are represented in Table I which gives, in the first column, the number of cubic centimeters of twice normal, normal, half and tenth normal solutions of the soluble chloride required to produce a precipitate or opalescence when added to 6.33 c.c. of a saturated solution of lead nitrate, and to this quantity of lead nitrate solution plus 3.66 c.c. of saturated solution of mercuric chloride. These quantities of lead nitrate and mercuric chloride are the amounts required to furnish the lead and chlorine necessary to form one tenth of a gramme molecule of lead chloride.

T A B L E I

Salt	2N c.c.	Conc.Cl ₂	N c.c.	Conc.Cl ₂	N/2 c.c.	N/10 c.c.
HCl	1.6					
HCl & HgCl ₂						
KCl	1.0	0.272	2.0	0.23	4.3	
KCl & HgCl ₂	1.3		2.6		5.5	
NaCl	1.0	0.272	2.0	0.23	4.7	88.no ppt.
NaCl & HgCl ₂	1.3		2.7		5.8	
NH ₄ Cl	1.9	0.276	2.0	0.23	4.2	70.no ppt.
NH ₄ Cl & HgCl ₂	1.3		2.68		6.5	
BaCl ₂	1.0	0.272	2.0	0.23	4.6	72.5
BaCl ₂ & HgCl ₂	1.2		2.4		5.5	
CaCl ₂	1.4	0.260	3.2	0.21	6.1	80.no ppt.
CaCl ₂ & HgCl ₂	1.7		3.4		8.0	
SrCl ₂	1.0	0.272	2.0	0.23	4.6	80.no ppt.
SrCl ₂ & HgCl ₂	1.3		2.6		5.7	
MgCl ₂	3.0	0.208	6.0	0.16	19.0	84.
MgCl ₂ & HgCl ₂	3.2		6.2			
CdCl ₂	.6	0.286	1.3	0.25	2.4	54.2
ZnCl ₂	1.0	0.272	2.0	0.23	4.2	37.8
ZnCl ₂ & HgCl ₂	1.1		2.2		4.5	

By reference to Table I it will be observed that practically the same holds true for sodium chloride, ammonium chloride, barium chloride, strontium chloride, and zinc chloride as for potassium chloride. In the case of calcium chloride about one half more of the solution is required to produce a permanent precipitate than in the case of the salts named, while three times as much magnesium chloride was used when lead nitrate alone was present. The presence of mercuric chloride does not seem to manifest as much of an effect in this case as in the other. If the amount of lead chloride be calculated from the amount of chlorine which has been added it will be found that the amount of lead chloride present in the solution is far in excess of the amount soluble in pure water according to the best determinations available. From Lichty's calculations at twenty-five degrees 1.0786 grammes of lead chloride are contained in 100 c.c. of solution, while according to Noyes the solubility of lead chloride in the presence of potassium chloride is very much decreased.

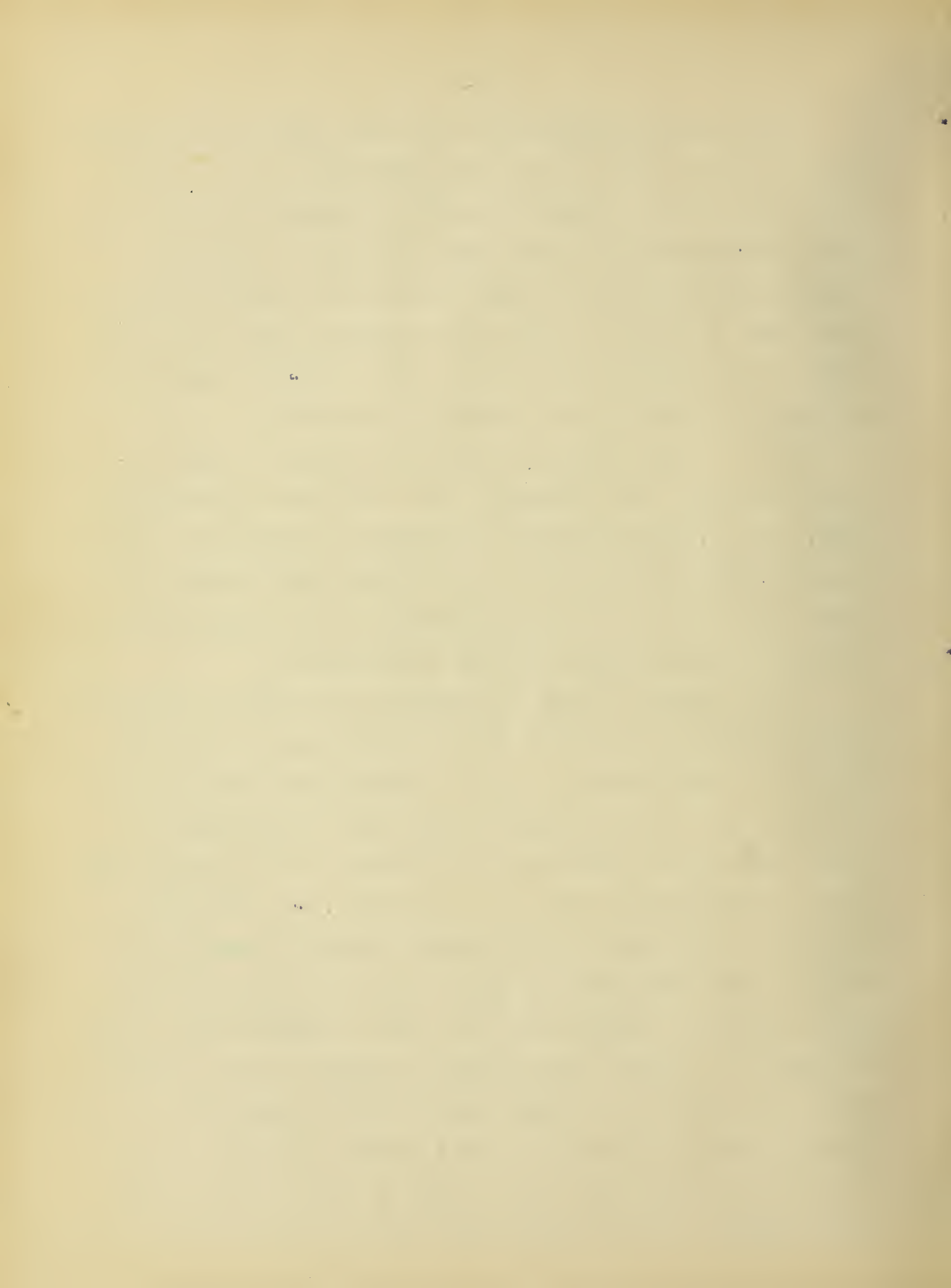
In our roughly quantitative determinations we introduce $\frac{d}{\Lambda}$ chlorine which was equivalent to 3.79 grammes of lead chloride in 100 c.c. of solution before any precipitate appeared, thus showing that we have, in solution, the constituents of lead chloride about three times as great in amount as there should be when the solution is saturated with lead chloride. By the addition of mercuric chloride we introduce the amount of chlorine sufficient to combine with all of the lead present and produce 2.778 grammes of lead chloride in eleven centimeters of solution, i.e. about 27 grammes in 100 c.c. of solution.



It will be recalled that only about one gramme of lead chloride is soluble in 100 c.c. at this temperature. It is therefore apparent that both potassium chloride and mercuric chloride separately and together, increase very materially the quantity of lead and chlorine which can exist in solution together. Whether they exist in solution in the form of lead chloride or of double salts of lead chloride and mercuric chloride, and of lead chloride and potassium chloride still remains to be proved.

From our roughly quantitatively measurements the same general statement is true concerning the other salts experimented with, that is, they all seem to increase the solubility of lead chloride. This conclusion is in opposition to the statement of Noyes that the solubility of lead chloride is decreased by the increase in concentration of these soluble salts.

It was thought desirable to determine the effect of the presence of different quantities of mercuric chloride upon the solubility of lead chloride. In order to make these solubility determinations, it was necessary to carry out the experiments in such a way that the solutions to be analyzed for the constituents should be saturated at the given temperature. As a saturated solution is a solution in which there appears, in equilibrium with the solid phase, all the salts which will dissolve at the given temperature. Unless the solid phase is present more of the salt may be in solution than enough to saturate at that temperature. The addition of a single crystal will, however, result in bringing down all the excess of salt present. In these experiments the precaution was taken to have an excess of the solid phase present, and by bringing every part of the solution in



contact with the solid phase for a period of eight hours at a temperature constant to a tenth of a degree we endeavor^{ed} to eliminate the error due to unsaturated or supersaturated solutions.

A water bath of about thirty litres capacity was equipped with an Ostwald automatic temperature regulator. The expansion of the contained liquid, in this case calcium chloride - any liquid with a high coefficient of expansion is suitable - shut off the gas supply by raising a column of mercury above the mouth of the ingress tube. On cooling, the contraction of the liquid lowered the mercury sufficiently to readmit the gas. The regulator could be made to keep the bath at any desired temperature and was sufficiently sensitive to record variations of a few hundredths of a degree.

The thermostat was enclosed in a wrapper of asbestos paper to protect it from drafts and to minimize the escape of the heat. For high temperatures, a layer of low melting parafine was kept on top of the water and effectually prevented heat radiation. The experiments were conducted under conditions such that the temperature of the bath was kept constant within from one to two tenths of a degree for eight hours. Standard thermometers showed that the temperature of the bath could vary three tenths of a degree for an hour without affecting the temperature of the solutions within the bottles.

The bottles were made to stand in a frame so placed that the level of the water came just to the necks. The revolution of a fan whose blades drove the water upward insured uniformity of temperature throughout the bath and kept the bottles in contact with the most recently heated water.

The solutions contained in the bottles varied from a saturated solution of lead nitrate to a saturated solution of mercuric chloride. Intermediate solutions contained saturated lead nitrate with definite and increasing amounts of mercuric chloride up to the point where two saturated solutions were in contact. This was accomplished in the following way: enough nitrate was dissolved in hot water to render the solution slightly supersaturated at the temperature of the bath. This solution was poured into the bottles on top of the mercuric chloride which had been previously weighed out. The first bottle contained no chloride, the second one gramme, the third two grammes, etc. In the ninth bottle enough mercuric chloride was placed to render the solution saturated with that salt alone, while in the tenth no nitrate appeared.

Several means for bringing every part of the solutions in the bottles in contact with the solid phase were worked upon but the one which seemed most practicable was to have the solutions agitated by individual stirrers. To this end a frame was made to cover all the bottles and into the neck of each was introduced a glass sleeve fastened through the frame. A number of screw stirring rods was made by taking twelve-inch glass rods of about an eighth of an inch diameter and flattening out about two inches at the end. While still hot these ends were twisted into the screw shape. After the stirrers were in the bottles, inch pulleys were put on and the rods kept in constant revolution from a counter shaft. The speed of revolution was about one hundred fifty per minute and was maintained from the time the solutions were put in the bottles until equilibrium at the desired temperature was established and the liquor ready to be drawn out.

The problem of removing the solutions from the bottles was met in the following way. Where the liquid and solid phases are so closely associated, any endeavor to draw out the liquid direct is likely to result in taking out the solid phase as well. To avoid any trouble of this nature, individual filters were prepared by drawing out the ends of half inch glass tubes and blowing the drawn end into the shape of a bell. A plug of cotton batting was forced into the bell and any solution which was to be drawn out must pass through this filter. Before being put into the bottles the strainers were heated to the temperature of the bath to prevent the cooling and consequent crystallization of the solutions.

The strainer was connected with a specially constructed burette by means of a short rubber tube so that the end of the burette projected down into the strainer for about two inches. This carefully calibrated burette had a capacity of thirty cubic centimeters and was graduated to twentieths of a centimeter.

A condenser jacket of such length as to include the entire burette from the side-neck delivery tube to the top, was held in place and rendered air tight by means of rubber tubes. A suction pump was used to draw water from a near-by bath, kept from two to five degrees warmer than the thermostat, through the jacket. After filling and emptying twice, the water was finally allowed to remain in contact with the burette and everything was ready for the withdrawal of the solutions. Every precaution had been taken to prevent the possibility of crystallization of the heavily saturated solutions at high temperatures. The burette and strainer were both warmer than the liquid to be abstracted and the only chance for cooling and consequent crystallization was in the side delivery tube.

This difficulty was obviated by winding the tube with a cloth soaked in hot water.

A small amount of the solution was drawn into the burette and allowed to run out through the delivery tube. Then the burette was filled but before any of the solution was collected about three cubic centimeters were allowed to run out to make certain that no products of crystallization might be present. Fifty cubic centimeters of the solution were run into a previously weighed flask for a specific gravity determination and fifteen cubic centimeters were run into a two hundred fifty centimeter graduated flask for dilution and the subsequent determination of the amounts of mercury and lead present.

As soon as all the solution required, had been drawn from a bottle the burette was taken down, washed with hot water, then alcohol and finally dried by drawing a current of air through it for a few minutes. It was then ready to be heated again and the process of extraction to proceed as before. This method ought to be reliable since the solutions have been kept stirred at a constant temperature for eight hours and equilibrium must have been established in that time. The solutions have been withdrawn without cooling and the definite amounts kept out of contact with the air until the determination^s of their components were made.

After a careful review of the several quantitative methods for determining the lead in solutions it seemed best to precipitate the lead as a sulphate and then to calculate the proportion of lead nitrate from the lead sulphate found. The two hundred fifty centimeter flask, containing fifteen centimeters of the solution in two hundred thirty-five centimeters of water, was shaken until the con-

tents were thoroughly homogeneous. Twenty-five centimeters were delivered from a burette and treated with one centimeter of concentrated sulphuric acid. The beaker containing the precipitate of lead sulphate was left on a hot plate for half an hour to drive off all the nitric acid. The solutions were not allowed to come to a boil on account of the volatility of the mercuric compounds as well as the danger of bumping from the heavy precipitate.

The solution was then filtered through a previously weighed, asbestos-lined, Gooch crucible and the precipitate washed with dilute sulphuric acid and finally with alcohol. The crucible was then kept in an air bath for two hours and when perfectly dried, weighed again. The difference in weights was the amount of lead sulphate present.

The determination of the mercury was more difficult than that of the lead. A solution could not be evaporated, the residue weighed and the amount of lead subtracted from such weight on account of the volatilization of the mercury compounds.

F.B. Hannay (Jour. Chem. Soc. 26, 565, 1873) gives a method for the volumetric determination of mercury which seemed reliable as modified by R.V. Tuson (Jour. Chem. Soc. 32, 679, 1877). As the lead had already been separated in the form of lead sulphate and washed with alcohol it appeared easy to follow his method by neutralizing the excess of acid with potassium carbonate. The slight opalescence was removed by titrating against a standard potassium cyanide solution. The difficulty in establishing the end point in this manipulation caused us to adopt the sulphide method.

A current of hydrogen sulphide gas was passed through the warmed filtrate from the lead precipitate and the black precipitate of

mercuric sulphide was collected in Gooch crucibles and weighed in the same manner as the lead.

In the following tables will be found the solubility determinations of lead nitrate in the presence of mercuric chloride at five different temperatures.

The heading of each column is self-explanatory.

T A B L E II

$\text{Pb}(\text{NO}_3)_2$ Temperature 21.8°C.

NO.	Wt.100 c.c.sol.	PbSO_4 in 15 c.c.sol.	\rightleftharpoons of PbSO_4 as $\text{Pb}(\text{NO}_3)_2$	$\text{Pb}(\text{NO}_3)_2$ in 100 c.c.sol.	G.in 100G. of water	Gm.Mol. $\text{Pb}(\text{NO}_3)_2$ 1.L.Sol.
1	137.9492	0.640	0.699	46.625	51.066	1.408
2	138.8988	0.652	0.713	47.543	51.110	1.436
3	140.2984	0.655	0.715	47.725	52.017	1.441
4	140.8806	0.654	0.714	47.645	51.706	1.439
5	141.5578	0.664	0.725	48.359	51.751	1.461
6	143.8164	0.661	0.724	48.273	51.549	1.458
7	143.2182	0.655	0.716	47.769	51.383	1.443
8	143.2080	0.655	0.716	47.739	51.695	1.442
9	142.3618	0.642	0.700	46.677	51.346	1.410
10	103.6106	- - -	- - -	- - -	- - -	- - -

T A B L E III

HgCl_2 Temperature 21.8°C.

NO.	HgS in 15 c.c.sol.	\rightleftharpoons of HgS as HgCl_2	HgCl_2 in 100 c.c. sol.	G.in 100G. of water	Gm.Mol. HgCl_2 1.L.Sol.
1	- - -	- - -	- - -	- - -	- - -
2	0.005	0.006	0.451	0.506	0.016
3	0.010	0.012	0.824	0.899	0.034
4	0.014	0.016	1.089	1.182	0.039
5	0.019	0.022	1.525	1.663	0.056
6	0.024	0.028	1.898	2.027	0.070
7	0.031	0.037	2.492	2.665	0.096
8	0.040	0.046	3.120	3.379	0.115
9	0.061	0.071	4.778	5.256	0.176
10	0.082	0.096	6.428	6.614	0.231



T A B L E IV

$Pb(NO_3)_2$ Temperature 29.3° C.

NO.	Wt. 100 c.c. Sol.	$PbSO_4$ in 15 c.c. Sol.	Δ of $PbSO_4$ as $Pb(NO_3)_2$	$Pb(NO_3)_2$ in 100 c.c. Sol.	G. in 100G. of water.	Gm. Mol. $Pb(NO_3)_2$ 1.L. Sol.
1	144.9809	0.750	0.819	54.651	60.502	1.651
2	145.7125	0.779	0.851	56.771	64.738	1.715
3	146.1933	0.780	0.833	55.577	63.121	1.679
4	147.3358	0.784	0.836	55.799	62.718	1.685
5	147.6908	0.778	0.850	56.690	64.773	1.712
6	149.5216	0.768	0.839	55.984	62.958	1.691
7	150.4184	0.760	0.831	55.399	61.720	1.673
8	149.5817	0.758	0.828	55.248	62.524	1.669
9	149.0134	0.754	0.823	54.913	63.566	1.659
10	104.6336	- - -	- - -	- - -	- - -	- - -

T A B L E V

$HgCl_2$ Temperature 29.3° C.

NO.	HgS in 15 c.c. Sol.	Δ of HgS as $HgCl_2$	$HgCl_2$ in 100 c.c. Sol.	G. in 100G of water.	Gm. Mol. $HgCl_2$ 1.L. Sol.
1	- - -	- - -	- - -	- - -	- - -
2	0.008	0.009	0.638	0.758	0.023
3	0.016	0.018	1.248	1.417	0.045
4	0.033	0.038	2.568	2.886	0.094
5	0.044	0.052	3.486	3.983	0.128
6	0.059	0.069	4.614	5.189	0.170
7	0.067	0.078	5.260	5.860	0.194
8	0.081	0.087	5.981	6.769	0.220
9	0.092	0.115	7.713	8.928	0.284
10	0.100	0.119	7.980	8.275	0.294

T A B L E VI

Pb(NO₃)₂ Temperature 40.3° C.

NO.	Wt.100 c.c.Sol.	PbSO ₄ in 15 c.c.Sol.	☆of PbSO ₄ as Pb(NO ₃) ₂	Pb(NO ₃) ₂ in 100 c.c. Sol.	G.in 100G.Gm.Mol. of water. Pb(NO ₃) ₂ 1.L.Sol.
1	145.8401	0.850	0.928	61.919	73.782 1.870
2	151.6318	0.866	0.946	63.070	72.065 1.905
3	151.2799	0.861	0.940	62.720	72.518 1.894
4	154.0134	0.864	0.943	62.931	72.234 1.901
5	155.8793	0.869	0.949	63.310	71.878 1.912
6	154.7430	0.860	0.939	62.640	71.719 1.892
7	154.3134	0.857	0.936	62.429	72.218 1.886
8	154.9459	0.852	0.931	62.079	71.805 1.875
9	155.4157	0.849	0.928	61.868	72.399 1.869
10	105.4544	- - -	- - -	- - -	- - -

T A B L E VII

HgCl₂ Temperature 40.3° C.

NO.	HgS in 15 c.c.Sol.	☆of HgS as HgCl ₂	HgCl ₂ in 100 c.c.Sol.	G.in 100G. of water.	Gm.Mol. HgCl ₂ 1.L.Sol.
1	- - -	- - -	- - -	- - -	- - -
2	0.013	0.015	1.042	1.191	0.038
3	0.026	0.031	2.070	2.393	0.076
4	0.050	0.059	3.961	4.546	0.146
5	0.057	0.067	4.490	5.097	0.165
6	0.061	0.071	4.762	5.452	0.175
7	0.069	0.081	5.439	6.292	0.200
8	0.082	0.096	6.412	7.417	0.236
9	0.104	0.121	8.093	9.191	0.298
10	0.112	0.131	8.743	9.040	0.322

T A B L E VIII

		Pb(NO ₃) ₂		Temperature	50° C.	
NO.	Wt.100 c.c.Sol.	PbSO ₄ in 15 c.c.Sol.	of Δ of PbSO ₄ as Pb(NO ₃) ₂	Pb(NO ₃) ₂ in 100 c.c.Sol.	G.in 100G of water.	Gm.Mol. Pb(NO ₃) ₂ 1.L.Sol.
1	151.6877	0.905	0.989	65.939	76.899	1.992
2	154.3284	0.915	0.999	66.646	77.034	2.013
3	154.4577	0.922	1.008	67.214	78.059	2.030
4	155.2902	0.923	1.008	67.235	80.012	2.030
5	157.6069	0.936	1.024	68.219	80.445	2.061
6	157.5018	0.934	1.021	68.087	81.094	2.057
7	157.6893	0.925	1.011	67.418	81.284	2.036
8	158.7872	0.920	1.005	67.046	80.026	2.025
9	160.7498	0.907	0.990	66.056	77.629	1.995
10	106.6190	- - -	- - -	- - -	- - -	- - -

T A B L E IX

HgCl ₂		Temperature	50° C.		
NO.	HgS in 15 c.c.Sol.	△ of HgS as HgCl ₂	HgCl ₂ in 100 c.c.Sol.	G.in 100G. of water.	Gm. Mol. HgCl ₂ 1.L.Sol.
1	---	---	---	---	---
2	0.015	0.017	1.167	1.349	0.043
3	0.032	0.037	2.513	2.966	0.092
4	0.051	0.063	4.023	4.787	0.145
5	0.060	0.070	4.585	5.420	0.169
6	0.067	0.078	5.260	6.251	0.194
7	0.094	0.109	7.330	8.858	0.270
8	0.102	0.119	7.961	9.502	0.293
9	0.123	0.143	9.587	11.240	0.353
10	0.147	0.172	11.473	12.065	0.423

T A B L E X

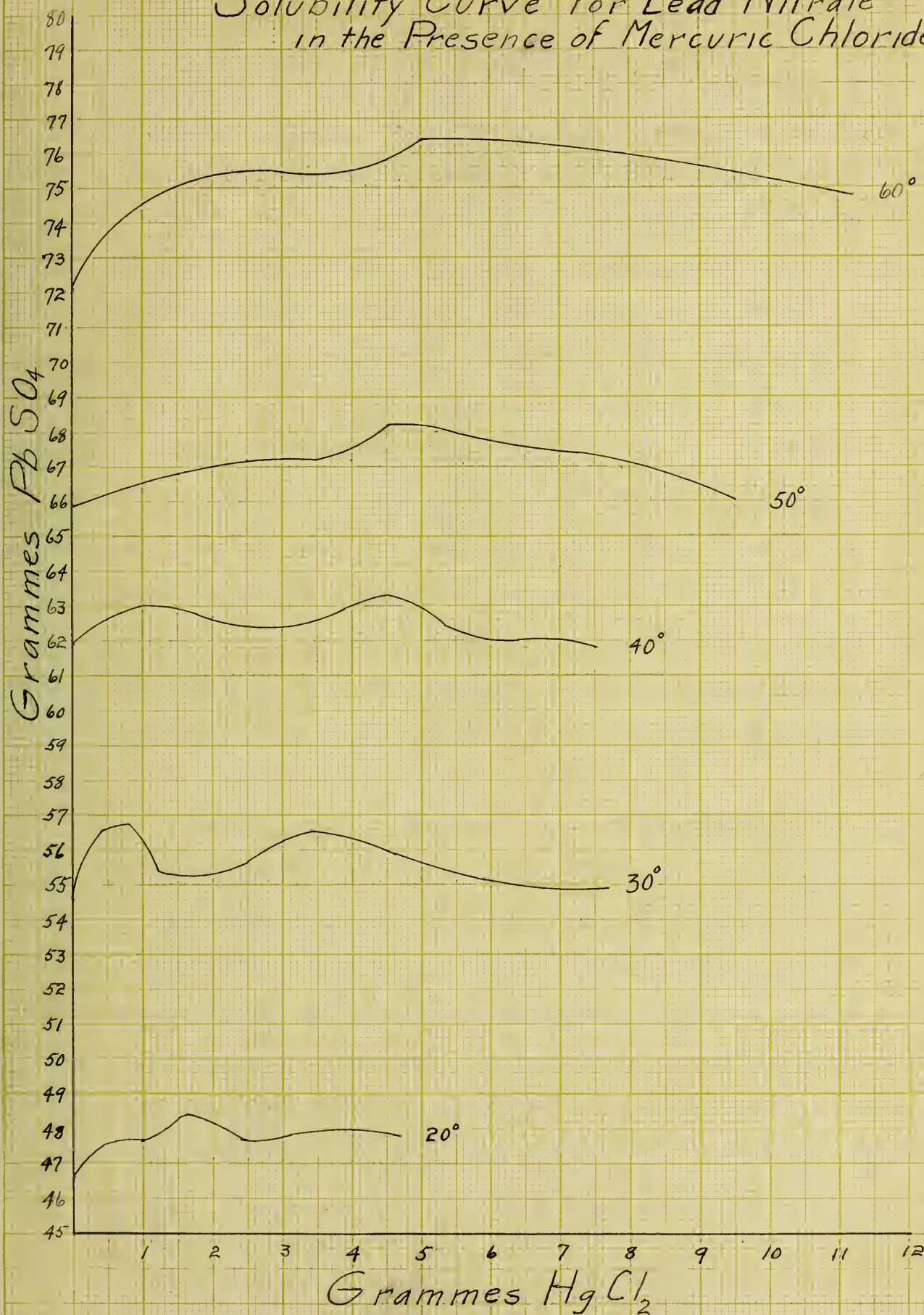
		$\text{Pb}(\text{NO}_3)_2$	Temperature	59.3° C.		
NO.	Wt.100 c.c.Sol.	PbSO_4 in 15 c.c.Sol.	Δ of PbSO_4 as $\text{Pb}(\text{NO}_3)_2$	$\text{Pb}(\text{NO}_3)_2$ 100 c.c.Sol.	G.in 100G of water	Gm.Mol. $\text{Pb}(\text{NO}_3)_2$ 1.L.Sol.
1	159.7709	0.990	1.082	72.152	82.348	2.179
2	161.5591	1.037	1.133	75.538	90.280	2.282
3	161.8892	1.038	1.134	75.662	91.431	2.285
4	161.3489	1.049	1.146	76.419	95.649	2.308
5	164.3688	1.023	1.119	74.511	88.207	2.251
6	165.2144	1.016	1.107	73.846	86.455	2.231
7	166.6767	1.008	1.101	73.441	86.827	2.218
8	166.3597	1.011	1.104	73.652	89.752	2.225
9	167.3848	0.999	1.092	72.814	87.344	2.199
10	106.0460	- - -	- - -	- - -	- - -	- - -

T A B L E XI

		HgCl_2	Temperature	59.3° C.	
NO.	HgS in 15 c.c.Sol.	Δ of HgS as HgCl_2	HgCl_2 in 100 c.c.Sol.	G.in 100G. of water.	Gm.Mol. HgCl_2 1.L.Sol.
1	- - -	- - -	- - -	- - -	- - -
2	0.030	0.035	2.350	2.808	0.086
3	0.044	0.052	3.470	4.194	0.128
4	0.064	0.075	5.035	6.302	0.185
5	0.069	0.080	5.385	6.375	0.198
6	0.076	0.083	5.953	6.969	0.219
7	0.111	0.129	8.653	8.126	0.319
8	0.136	0.159	10.646	12.973	0.392
9.	0.144	0.168	11.206	13.442	0.413
10	0.158	0.184	12.303	13.095	0.454

From an examination of the data in the accompanying tables, the change in the solubility of lead nitrate in the presence of mercuric chloride does not seem to be very great. The variations are very slight and consequently very accurate experimental work is necessary throughout in order to show the change in the solubility. There seems to be a slight increase in the solubility of lead nitrate with the addition of mercuric chloride which reaches its maximum when two to three grammes of mercuric chloride is present in one hundred centimeters of the solution. This becomes more apparent upon examination of Plate I.

Solubility Curve for Lead Nitrate in the Presence of Mercuric Chloride





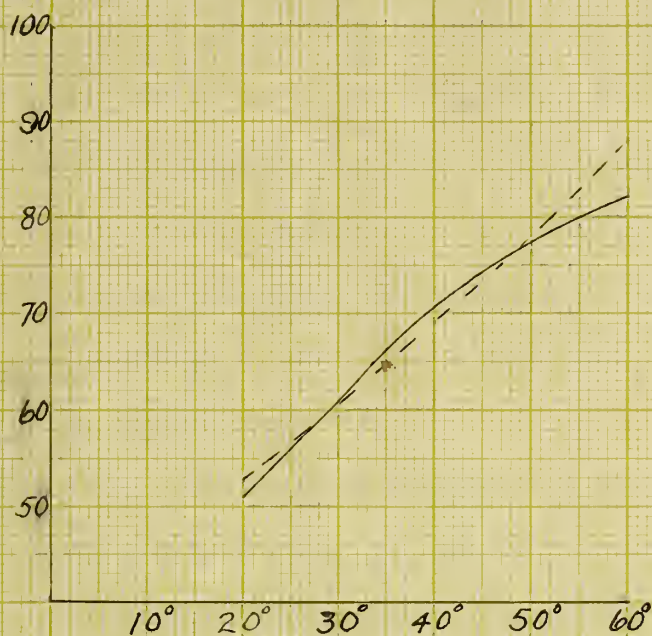
The grammes of lead nitrate in one hundred cubic centimeters are represented by the ordinates while the abscissae represent the grammes of mercuric chloride present. By the addition of mercuric chloride the solubility of the lead nitrate increases slightly and then decreases until, in solutions saturated with mercuric chloride, the amount of lead nitrate present is practically the same as the amount present in pure water, thus showing that at certain concentrations there is a maximum solubility of lead nitrate in the presence of mercuric chloride. In the case of the solubility of lead chloride in the presence of hydrochloric acid the reverse of this has been noticed, i.e., the lead chloride decreases in solubility on the addition of hydrochloric acid until a certain concentration is reached when the solubility increases again upon the addition of more hydrochloric acid. In this case there is a minimum value for lead chloride in the presence of hydrochloric acid.

From the published determinations on the solubility of lead salts and of mercury salts one is impressed with the lack of agreement of the investigators. The values assigned vary as much as twenty-five to thirty percent from each other. This seems to indicate that the determination of the presence of the quantity of these substances in solution is not as easy a task as would naturally be expected. At the present time we do not seem to have sufficiently accurate data on the solubility of the lead and mercury salts.

Solubility of Lead Nitrate

Expressed in grammes at T°

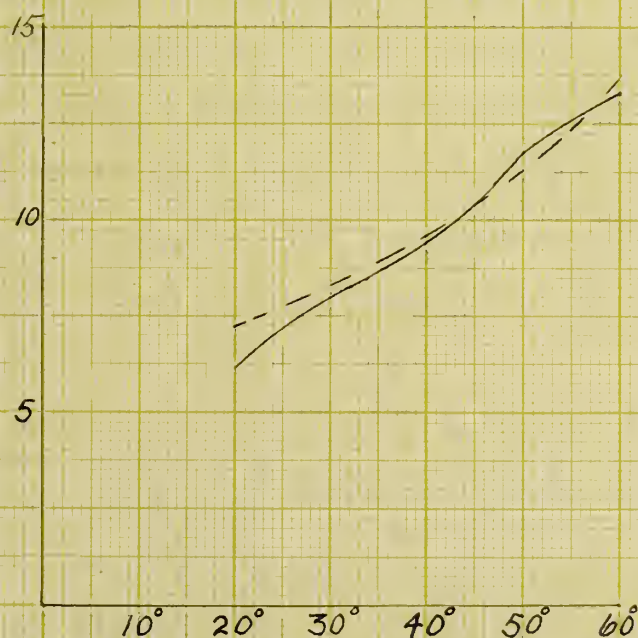
100 CC SOLUTION



Solubility of Mercuric Chloride

Expressed in grammes at T°

100 CC SOLUTION





On Plate II is represented by full line, my determinations of the solubility of lead nitrate and mercuric chloride over a range of temperature from twenty to sixty degrees. The dotted lines on this plate represent apparently the best determinations of the solubility of these two salts that we have been able to find in the literature. Although our values are not exactly the same, throughout the whole range of concentration yet they agree fairly well with the other determinations.

We have shown from a series of roughly quantitative determinations that if lead chloride is produced synthetically in a solution by adding to lead nitrate solution a soluble chloride, that the amount of lead chloride which can be produced in this way before a precipitate forms, is very much in excess of the amount of lead chloride soluble at the given concentration and temperature.

Noyes (Zeit. Phys. Chemie IX, 623, 1902) has shown that in the presence of the chlorides of the alkalies, the alkaline earths and some of the heavy metals, that the solubility of lead chloride diminishes with an increase in the concentration of these chlorides and from his determinations the amount of the lead chloride which can be dissolved in the presence of these chlorides is very much less than what appears possible to be produced synthetically.

We have shown that in the case of addition of potassium chloride to lead nitrate solution, the constituents which represent about three times the quantity of lead chloride that can remain in solution, can be added before a precipitate of lead chloride appears. This amount is increased about one third if mercuric chloride be present. The amount of chlorine which can be added in the form

of the soluble chlorides before a precipitate appears seems to be about one tenth of the amount necessary to react with all of the lead which is present.

Further, it seemed to be immaterial whether twice normal, normal, or half normal solutions of these alkali chlorides were used, as the precipitate of lead chloride appeared when almost exactly the same quantity of chlorine had been introduced by these solutions, that is, it took twice as much of the normal as of the double normal, and twice as much of the half normal as of the normal to produce the precipitate of lead chloride.

From our quantitative determinations it appears that the solubility of the lead nitrate is slightly affected by the presence of mercuric chloride. The solubility increases, reaching a maximum and then decreases to practically the solubility of lead nitrate in pure water, in the solution saturated with mercuric chloride. The maximum solubility of lead nitrate differs with the temperature varying from about two grammes of mercuric chloride at twenty degrees to about five grammes at sixty degrees.





